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COMBINED HYDROPHOBIC / OLEOPHOBIC MEMBRANE SEPARATION AND EXTRACTION FOR FUEL TREATMENT

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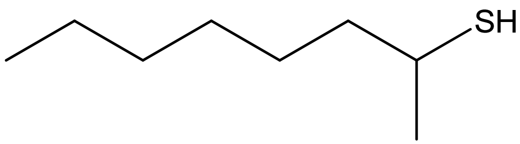
CRDF Project Overview

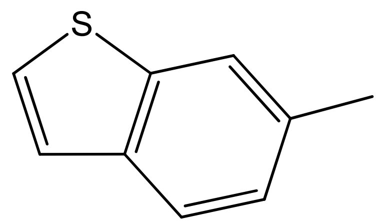
- Overall goal: Generate data to enable evaluation of portable fuel treatment technologies
- Application focus
  - Sulfur removal from diesel, primarily for ground or stationary power applications
  - Secondary focus on sulfur removal from jet fuel
- Technical components
  - Compact liquid-liquid extraction based on forced coalescence membranes
  - Reactive adsorption under mild conditions
  - Characterization of fuel products
  - Predictive tools for process performance

Sulfur in Fuels

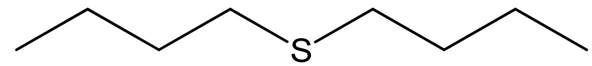
Mercaptans (Thiols)



Thiophenes (and benzothiophenes)



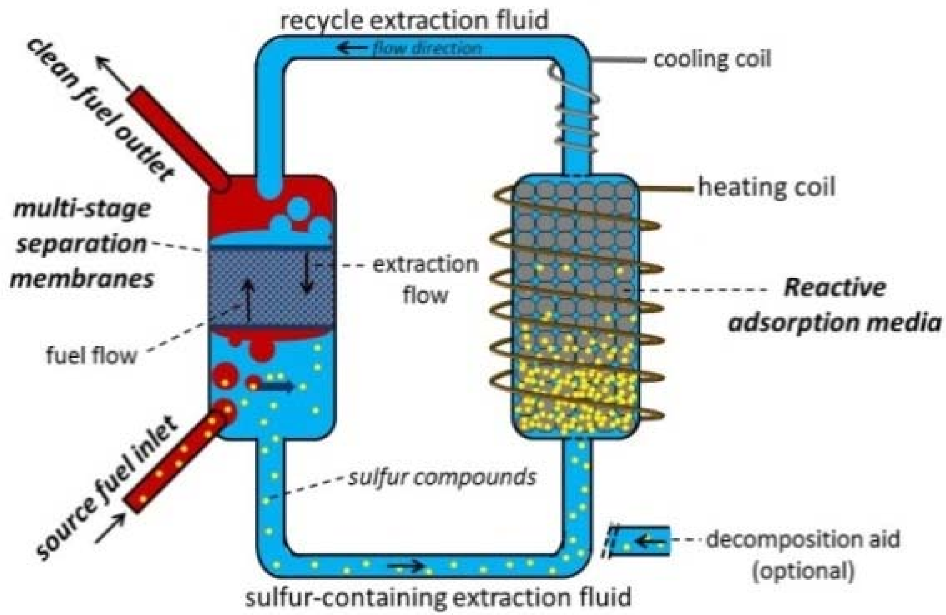
Sulfides

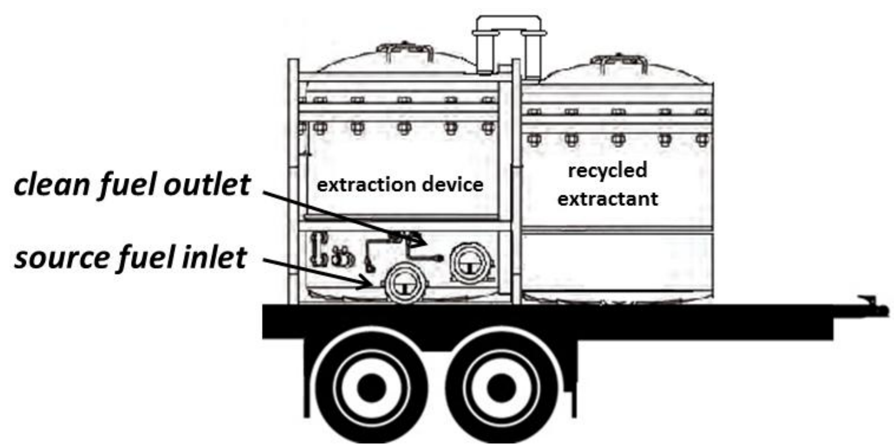


The presence of sulfur in fuels leads to many detrimental effects:

- Coking on rocket engine injector plates
- Deposit formation in hypersonic cooling channels
- Clogging of diesel engine fuel-injectors
- Fouling of automobile catalytic converters
- SO_x emissions
  - Environmental pollution
  - Corrosion issues on military equipment

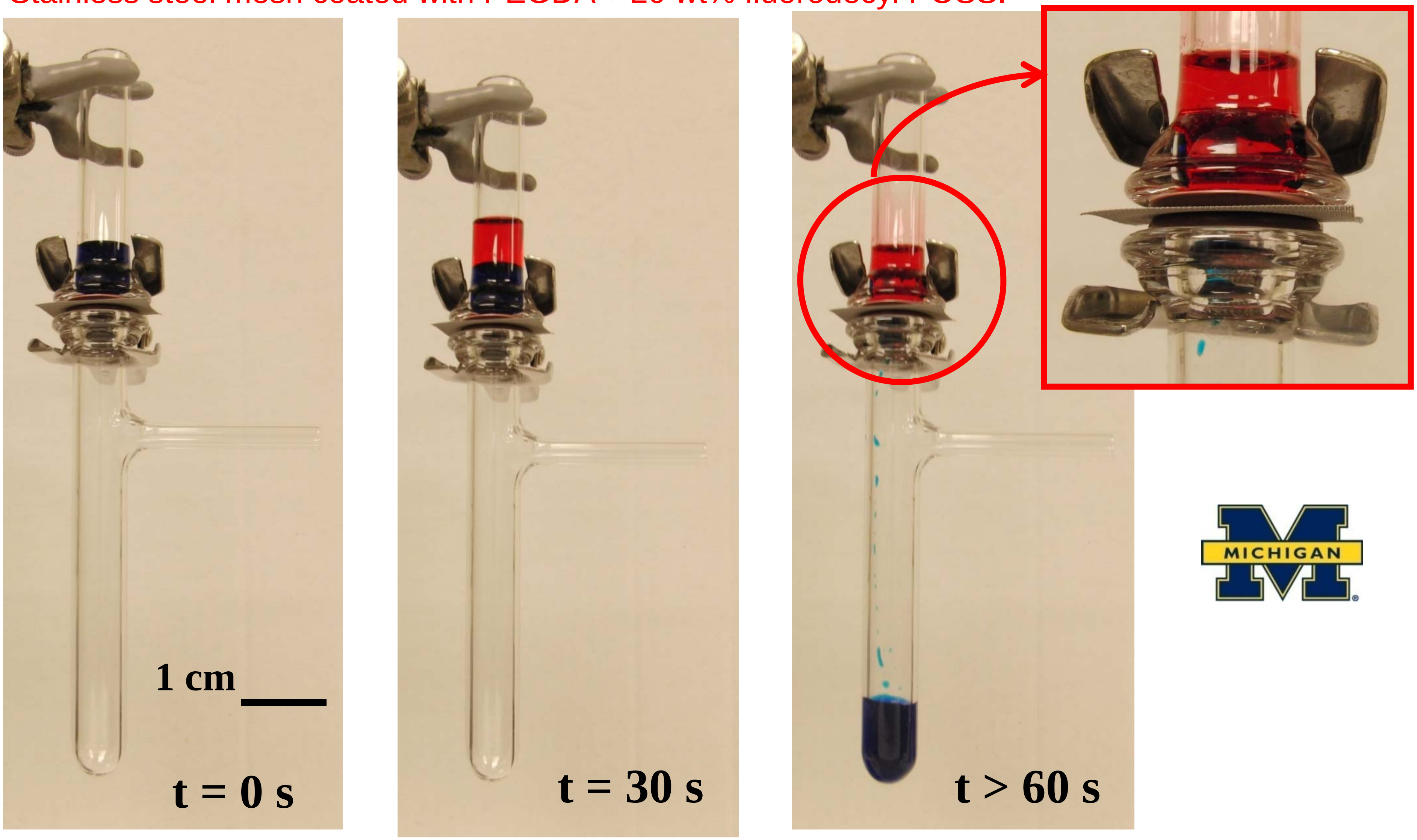
Overall Process





Water-Adhering Surface with Oil Repellence Separate Water from Oil

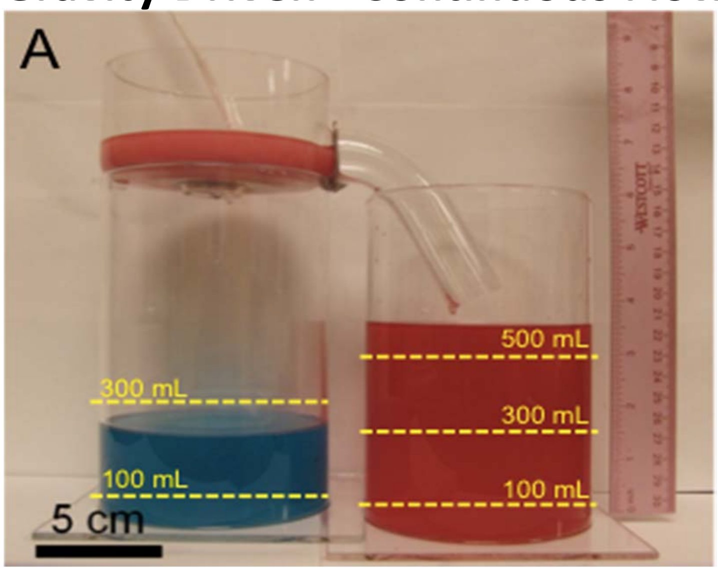
Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.



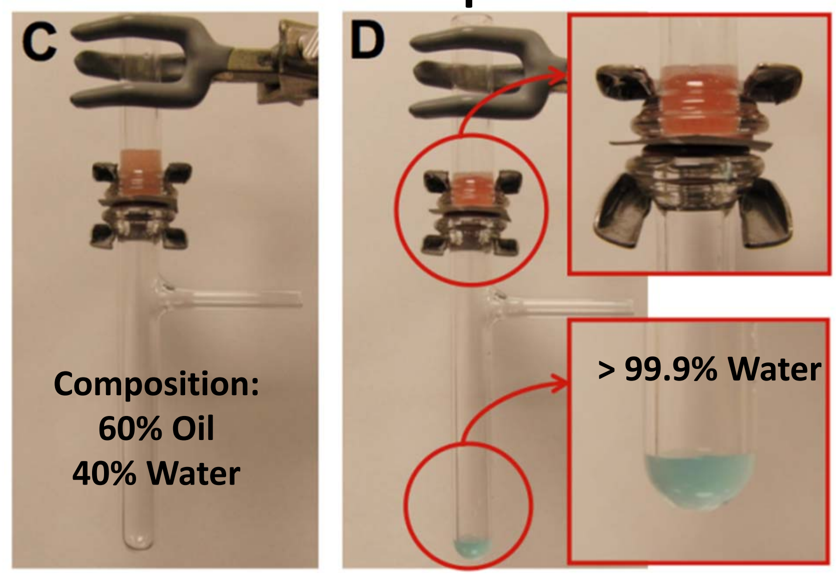
Separation via Forced Coalescence

- **Combine two mutually exclusive adherent / repellent surfaces; coalescence of phases caused by droplet redirection rather than merging; small droplets take longer to merge but bounce readily**
- **Result: a simple apparatus for the gravity driven, *continuous* separation of oil-water emulsions, proving that coalescence can be "short circuited"**
- **1 US patent, 1 application**

Gravity Driven - Continuous Flow



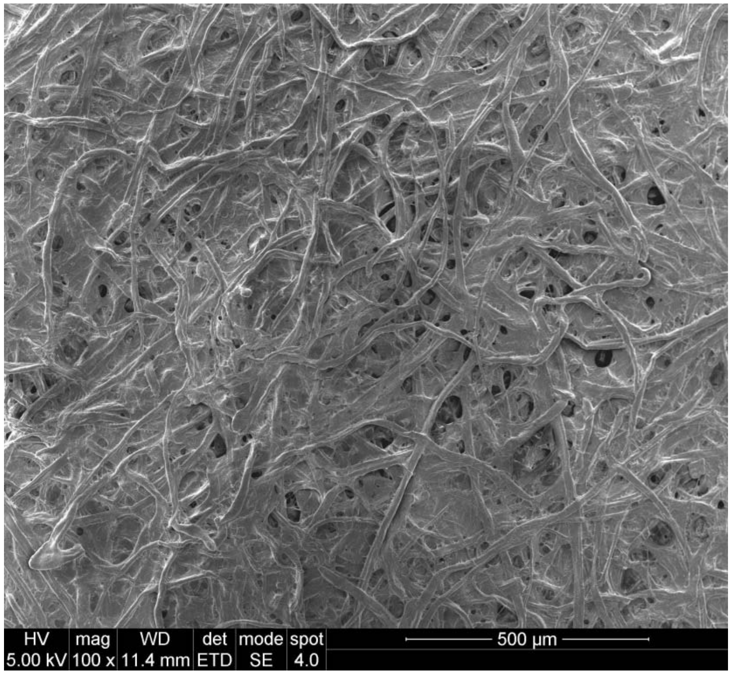
Emulsion Separation

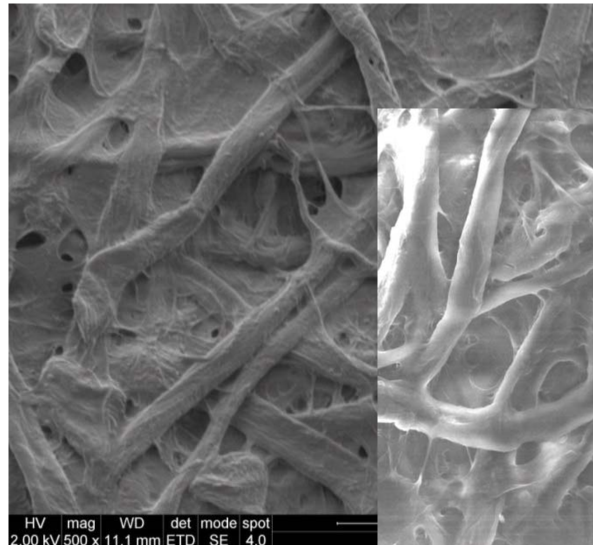


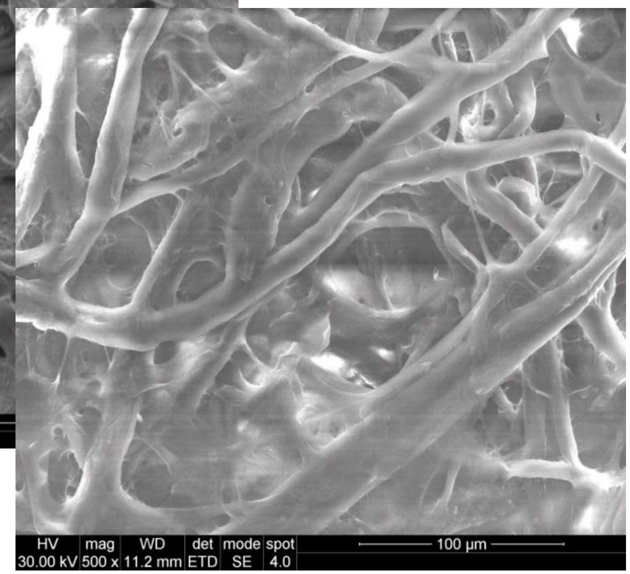
In collaboration with Prof. Anish Tuteja at the University of Michigan.

Nature Communications, **2012**, *3*, Article number: 1025 DOI: doi:10.1038/ncomms2027

Example Membrane (Hydrophobic): Whatman Phase Separator

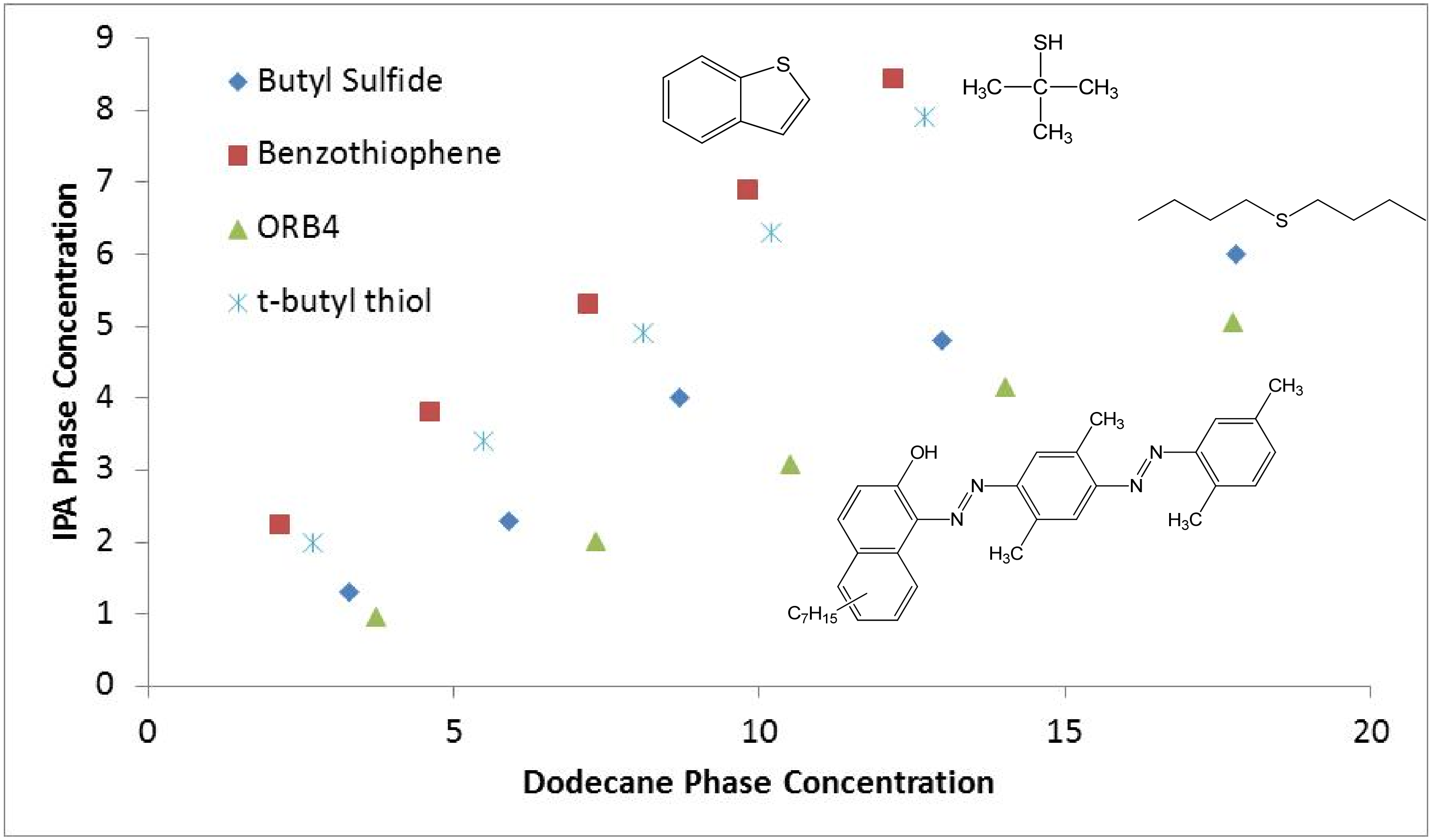






- These surfaces have ~10 µm roughness, ~10 µm fibers, and ~15 µm pores, with a wide range of pore sizes and re-entrant features. The surface energy appears to be around 26 mJ/m^2.
- Testing of hydrophilic membranes showed that pore sizes below ~5 µm result in high operating pressure drops and mechanical failure at >~2 gal / min / ft^2.
- Current hydrophilic membranes from Hygratech have ~25 µm pores, can withstand at least ~ 5 gal / min / ft^2, and have been 100% effective at separation.

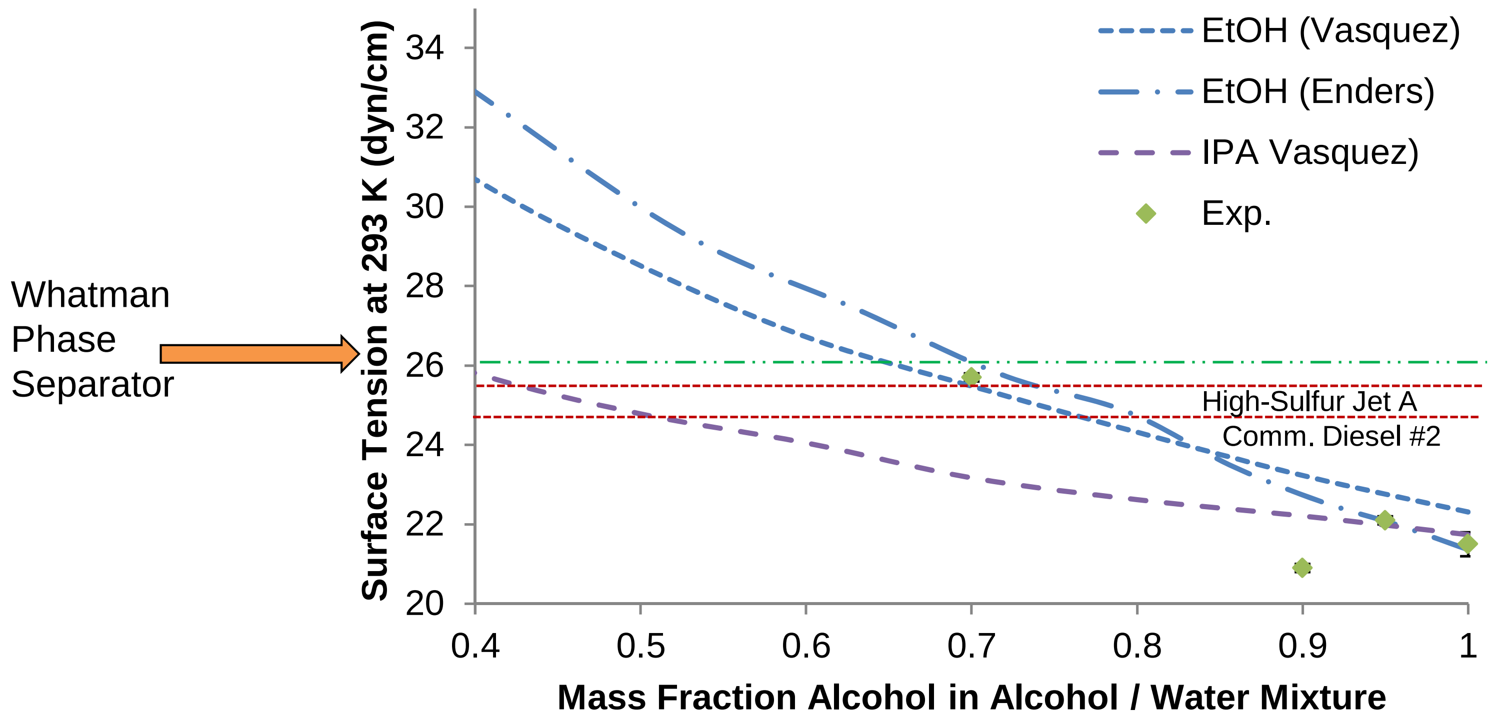
Equilibrium Curves for Extraction



The slope of these lines is the partition coefficient (K). K > ~0.1 for a feasible extraction process.

Equilibrium curve for compounds extracted from dodecane with IPA:water 10:1 v:v ratio

Extraction Media Selection

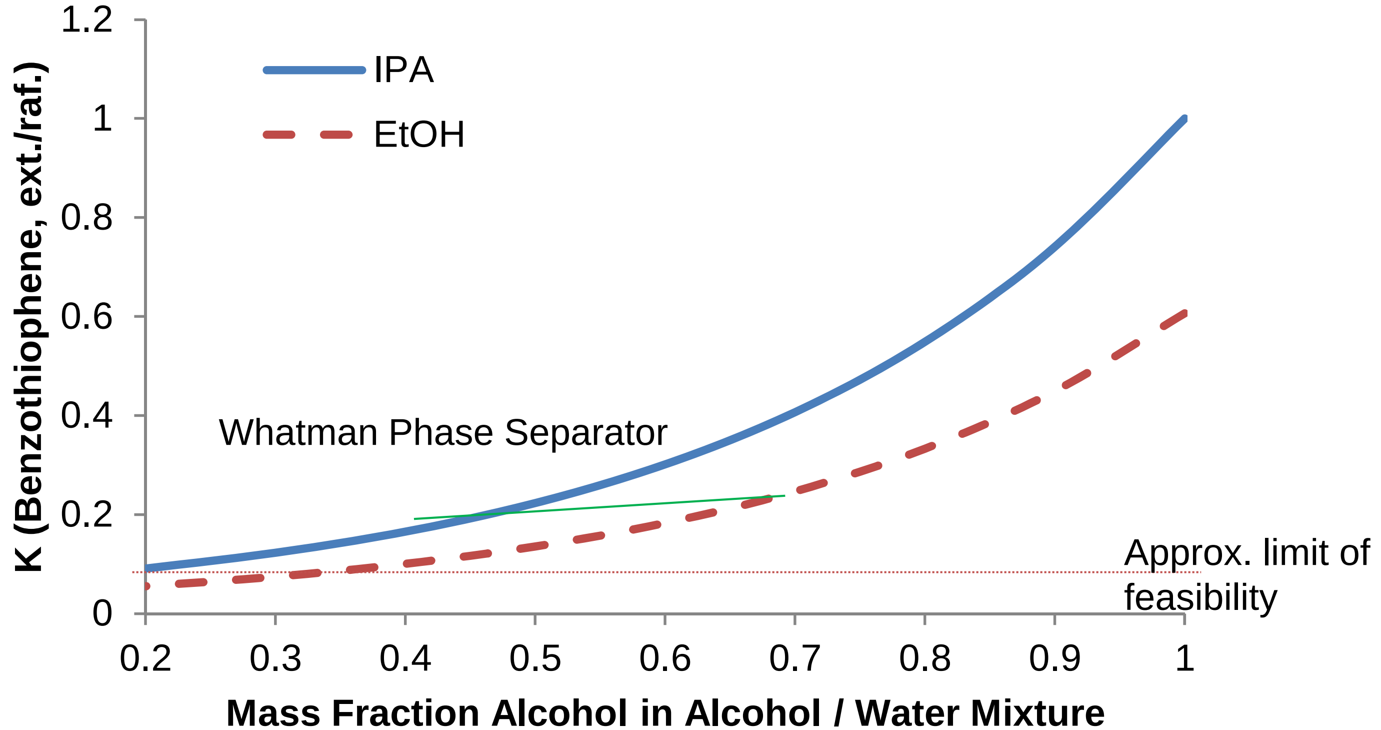


Limiting factor in extraction fluid selection is surface tension (must exceed that of all potential fuels to be utilized) when operating at flow rates high enough that phases do not coalesce within a single stage.

Membrane surface energy must lie between the surface tension of the extraction fluid and that of the fuel to be treated.

Sources: S. Enders, H. Kahl / Fluid Phase Equilibria 263 (2008) 160–167; Vasquez et al. J. Chem. Eng. Data (1995), 40, 611.

Extraction Media Selection

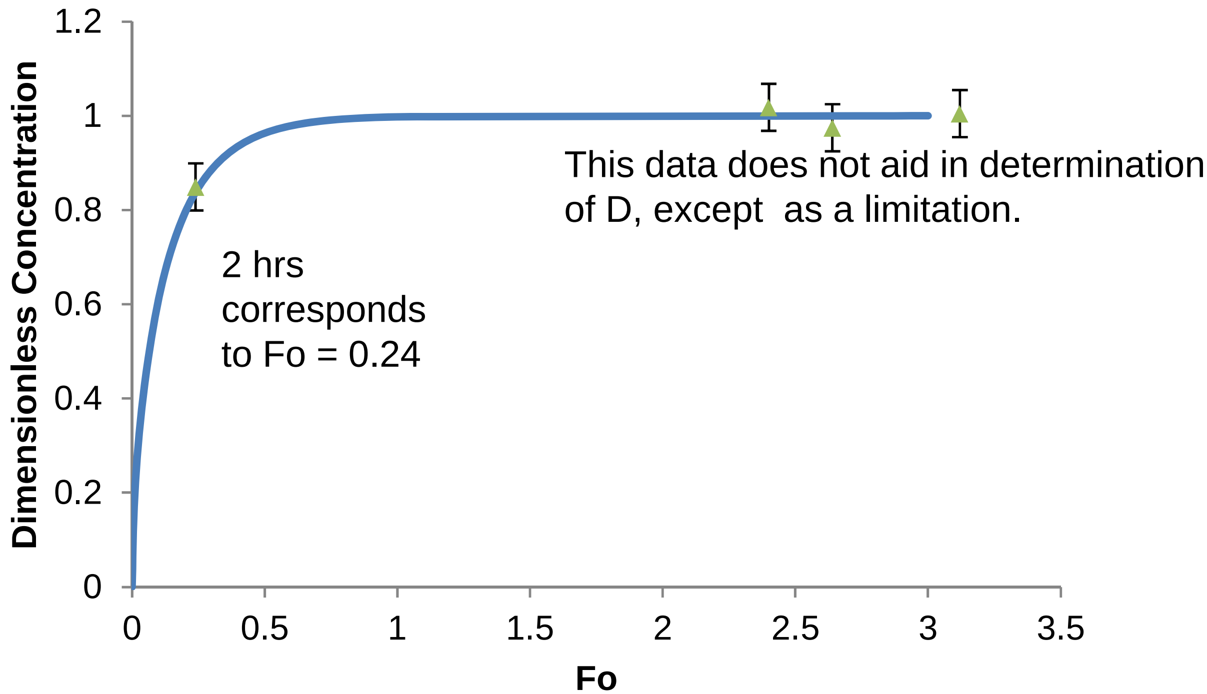


Increased water content results in less efficient extraction (lower K)

Because of surface tension constraints, the design choice falls along the thin lines indicated, not along the horizontal axis

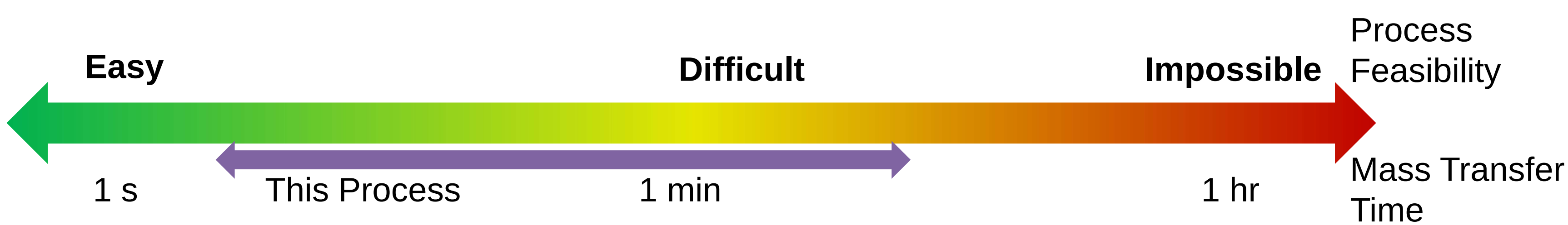
Actual design trade is relatively insensitive to alcohol choice

Diffusion Coefficient Calculations

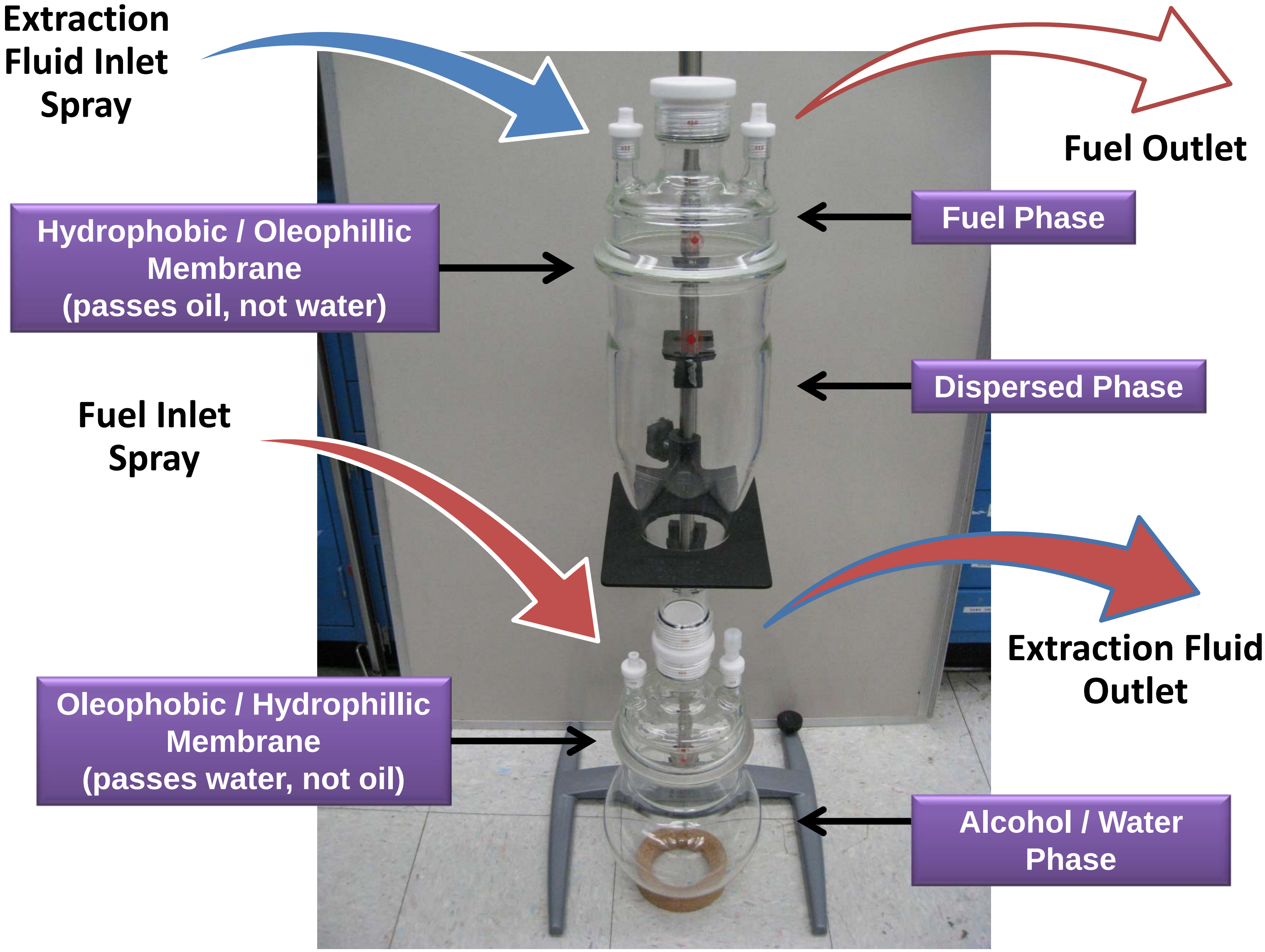


Fo = D t / L^2; in this case L = 0.97cm, solving for D yields 3 (±1) x 10^{-5} cm^2 / s

This value implies that for ~1 mm droplets, mass transfer will take ~30 s.



Laboratory Demonstration Extraction Apparatus



Extraction of Sulfur from RP-1

Sulfur Compounds by GC-SCD (Sulfur Speciation)	Concentration (ppm)
C2 Thiophenes	<0.1
C3-C4 Thiophenes	1.6
C5 Thiophenes	6.3
C6 Thiophenes	6.1
C7 Thiophenes	5.8
C8-C9 Thiophenes	4.9
C10 Thiophenes	1.3
C11 Thiophenes	0.9
C12+ Thiophenes	2.0

Standard Grade RP-1
(Errors are ±0.3 ppm**)**

Sulfur Compounds by GC-SCD (Sulfur Speciation)	Concentration (ppm)
C2 Thiophenes	0.3
C3-C4 Thiophenes	1.4
C5 Thiophenes	3.7
C6 Thiophenes	3.5
C7 Thiophenes	4.1
C8-C9 Thiophenes	2.9
C10 Thiophenes	0.6
C11 Thiophenes	0.6
C12+ Thiophenes	<0.1

Standard Grade RP-1 after extraction with 10:1 IPA water in extraction apparatus

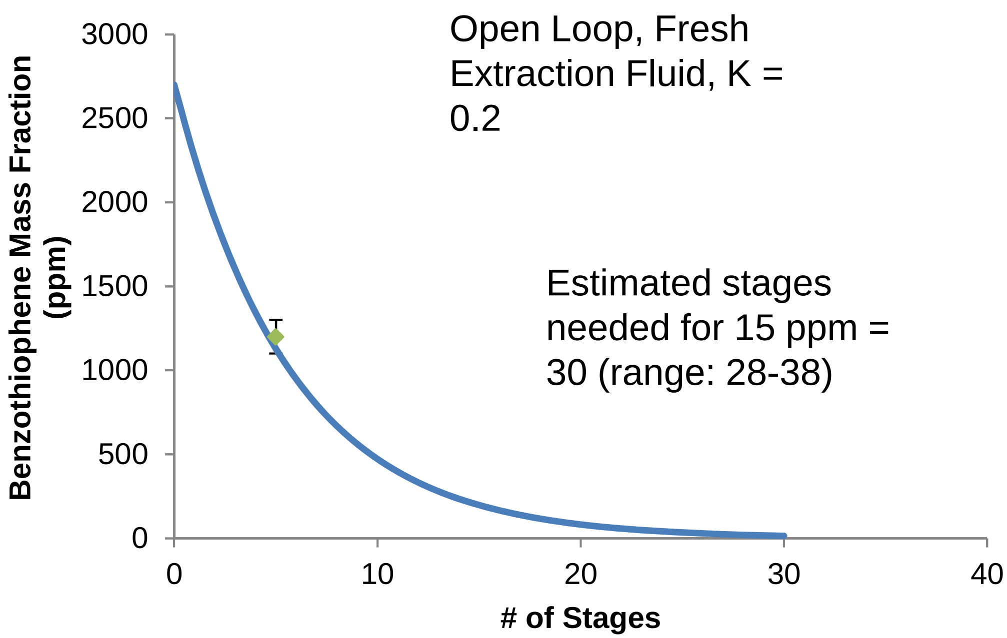
Extraction of RP-1: Effects on Composition

	POSF 11820 BG1121GP04 (untreated baseline)	POSF 11859 (treated w/ 10-15% IPA)	POSF 11860 (treated + salt water wash)	POSF 11861 (treated + salt water wash)
Alkylbenzenes (wt%)	0.49	0.39	0.47	0.47
Alkylnaphthalenes (wt%)	0.73	0.20	0.23	0.23
Cycloaromatics (wt%)	1.14	0.32	0.39	0.39
Total Aromatics (wt%)	**2.36**	**0.91**	**1.09**	**1.08**
Isoparaffins (wt%)	**34.96**	**30.10**	**33.84**	**33.84**
Normal Paraffins (wt%)	**8.93**	**5.70**	**6.39**	**6.40**
Monocycloparaffins (wt%)	**33.45**	**32.02**	**35.15**	**35.73**
Dicycloparaffins (wt%)	**18.24**	**18.26**	**21.13**	**20.42**
Tricycloparaffins (wt%)	**2.06**	**2.10**	**2.36**	**2.50**

Data provided by AFRL/RQTF

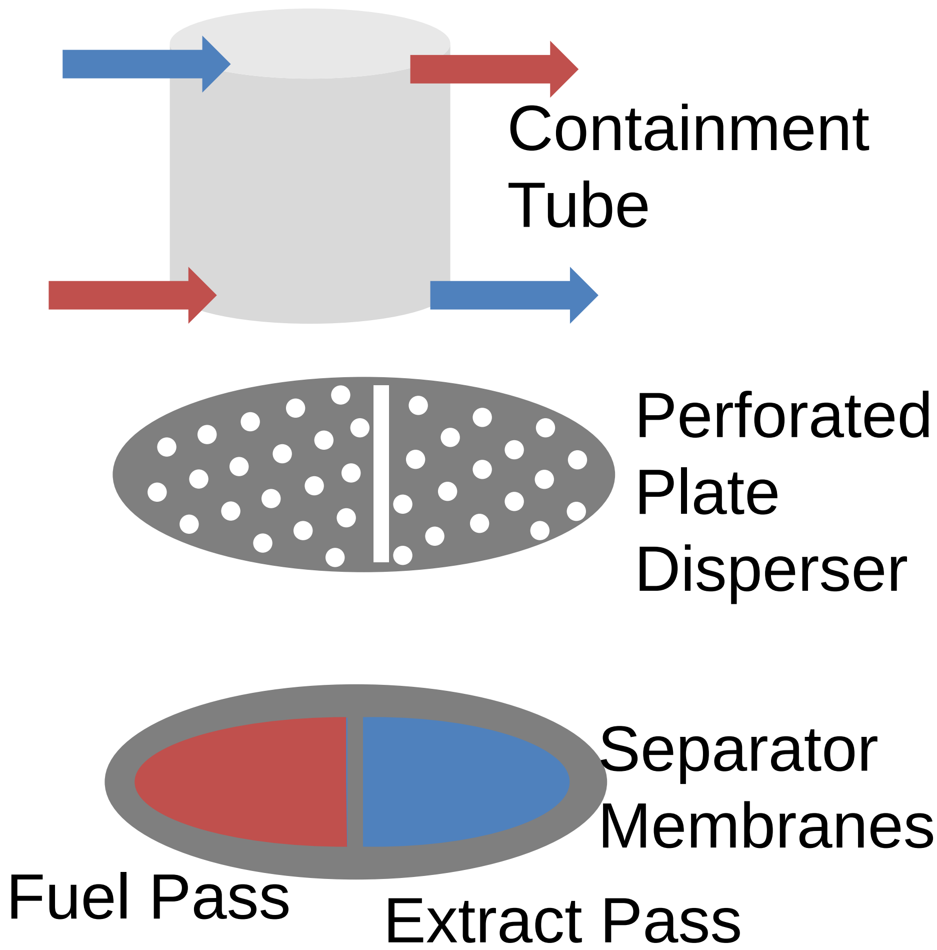
Extraction of Sulfur from Diesel #2

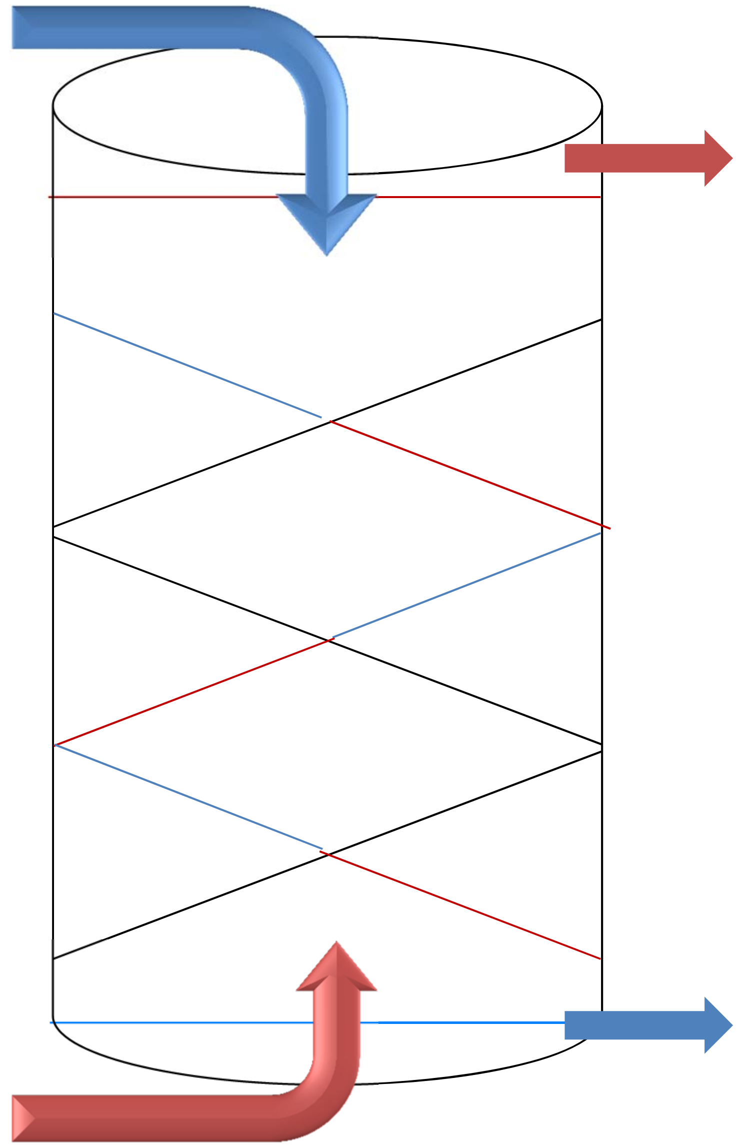
Parameter	Value
Input Fuel Source	Diesel #2 procured at Kramer's Junction, CA
Contaminant	Benzothiophene
Initial Contaminant Level	2700 ± 100 ppm
Final Contamination Level	1200 ± 100 ppm
# Passes	5
Expected Extraction Efficiency per Pass	K = 0.2



- Key question = how does extraction curve for other components compare to that of benzothiophene?

Scale-Up of Liquid/Liquid Extraction





~42” high x 6” dia., 50 GPH each phase

Summary

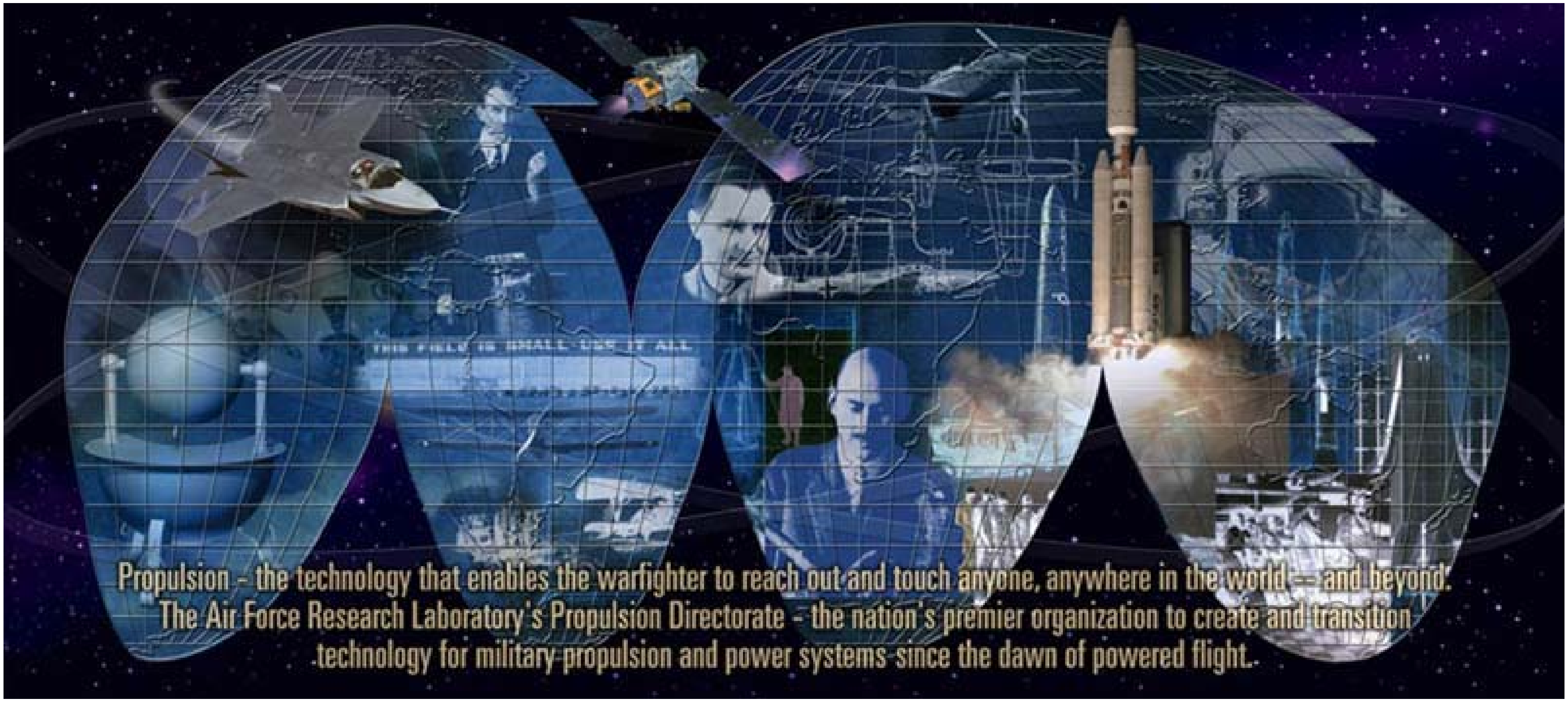
Liquid-liquid extraction processes that combine hydrophobic and oleophobic membranes offer a new route to fuel treatment

The required surface energies of the hydrophobic membranes (25 – 30 mJ / m^2) are the limiting factor in selection of alcohol : water extraction fluids. The attainable partition coefficients for typical sulfur contaminants are marginal for operation of a portable fuel treatment apparatus

Sulfur speciation data to date show no major differences in partition coefficient among the most common sulfur contaminants found in kerosene fractions

The process has so far been demonstrated with rocket fuel (RP), jet fuel (Jet-A) and diesel fuel (Commercial Diesel #2)

Key parameter to be determined: cost / feasibility estimates for process that supplies acceptable quality fuel from a given range of input sources, as a function of process scale



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